

Thermally Stimulated Depolarization Currents in Tri-ethyleneglycol Doped poly (methyl acrylate) Film Electrets

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ABSTRACT

Thermally Stimulated Depolarization Currents in tri-ethyleneglycol doped poly (methyl acrylate) (PMA) film (25 μ m thickness) was measured under various polarizing conditions. It was found two current maxima one at lower temperature (β -peak) and the other centred at higher temperature (α -peak). The magnitude of peak currents has been found to increase with increase in polarizing fields. The activation energy for the β -peaks is the same for field dependent TSDC thermograms. It is also amenable to special doping mechanisms so that the electronic properties can be modified through the variation of the number of electrons or protonic acid doping. In summation, PMA exhibits a high potential for several technological applications. So by looking the Importance of this polymer we are reporting here some modified polymer and its TSDC for various applications.

Keywords: TSDC, tri-ethyleneglycol, poly (methyl acrylate), α and β relaxation, space charge.

1. INTRODUCTION

Polymer materials have long been considered to be good insulators, because their predominant covalent bonds exhibit low electroconductivity. However, in the

1970's, it was found that when the linear polyenes and hetroaromatic polymers were doped by electrochemical or ion implantation methods, their electrical conductivity increased dramatically. The charge storage properties of polymers can

be considerably modified by impregnating them with some impurity¹⁻⁴. This effect has been attributed to the formation of charge transfer complexes between electron donors and electron acceptors. Several researchers have studied the charge storage and transport phenomena in polymer electrets by means of techniques based on thermal stimulation. Thermally Stimulated Depolarization Currents (TSDC) is useful in understanding the dielectric relaxation and in elucidating molecular parameters, thermal stability, relaxation times, activation energies, etc.⁵. TSDC analysis of a polarized dielectric is commonly used to get a insight into its charging process. It also provides useful information about the molecular motion in dielectrics⁶⁻⁸. Methyl methacrylate soon became the most important member of the acrylic family. The industrial applications of solutions or emulsion of acrylic ester polymer as coating or impregnates are many and varied. The inherent stability, durability and pigment binding characteristics of acrylic polymers have been important factors in selection of such systems in various coating applications such as in leather and textile finishing. Acrylic ester emulsion polymers are used in the paper industry as pigment binders, saturants, fibers and wet-end additions for high strength paper⁹⁻¹². Biomedical applications of acrylate based hydrogels include soft contact lenses, artificial corneas, soft tissue substitutes and burn dressings. Furthermore, the application of hydrogels to a variety of substrates leads to the production of thrombo-resistant coatings, catheters or blood detoxicants. Hydrogels are impregnated with biologically active agents, such as antibiotics, enzymes, contraceptives, drug antagonists, anticancer

drugs etc. and may serve as systems for the controlled release of the agents absorbed to a specific size of the body^{13,14}. So we have attempted to design a new doped poly (methyl acrylate) film electrets with modified properties by using thermally stimulated discharge.

2. EXPERIMENTAL DETAILS

Commercial Methyl acrylate always contains impurities, such as acrylic acid and ethylene glycol diacrylate (EGDA). Purification has to be done to remove diacrylate and acrylic acid. The presence of diacrylate leads to crosslinking and in the presence of large amounts of acrylic acid, no polymerization is observed. Therefore, polymerizations of unspecified or poorly purified monomer may be both incomplete and slow or lead to insoluble solids. MA (Acros, 97%) was dissolved in water (25% by volume) and the solution was extracted 10 times with hexane to remove diacrylates. The aqueous solution was then salted (200g of NaCl / L) and the monomer were separated from the aqueous phase by ether extraction (4 times) to remove acrylic acid. Finally, MgSO₄ (3 wt %) drying agent was used to remove traces of water before evaporation of the ether phase in a rotary evaporator. The purified monomer was distilled under vacuum immediately prior to use for polymerizations. Methanol, carbon tetrachloride (Merck), hexane (Merck), diethyl ether (Riedel de-Haen), benzyl chloride (Aldrich 99%) were all reagent grades and used without further purification. 2, 2'-bipyridine (Fluka), benzoyl peroxide (Merck), CuCl (Riedel de-Haen) were all reagent grades and used without further purification and polymerisation. I R

characteristics by using Nicolet 510 FT-IR Spectrometer. NMR Spectra of monomer and polymer were taken on an Ultrashield 400 MHz Digital NMR Bruker. SEM Micrographs took by JSM 6400 JEOL. The thickness of thin films of doped Poly (methyl acrylate) film (25 μm) Model CD-8"P made by Mititoyo Corporation.

3. RESULT AND DISCUSSION

Figure 1 shows the effect of various polarizing fields on TSDC characteristics of tri-ethyleneglycol doped poly (methyl acrylate) (PMA) samples polarized at polarizing temperature 40°C with 05, 10 and 15MV/cm polarizing fields. Its characteristics consist of two current maximas one at lower temperature (β -peak) and the other centred at higher temperature (α -peak). The magnitude of peak currents has been found to increase with increase in polarizing fields. The activation energy for all β -peaks is almost the same for field dependent TSDC thermograms (Table 1). However, for high field values sometimes the current is decreased in magnitude. The α -peak is shifted towards lower temperature side with increasing values of polarizing field. Figure 2 shows TSDC spectra's of doped PMA samples poled at given temperature of 40°C, 60°C, 80°C and 90°C at constant electric field 10MV/m. The peak current for all samples of doped PMA is found to be poling temperature dependent. α -peak is shifted towards higher temperature side with increasing values of poling temperature. The electrification of polymers takes place due to one or more of the following mechanisms operative simultaneously when it is subjected to dynamical, mechanical or thermal treatment with or without the static

electric fields: (i) space charge injected into the dielectric by surface breakdown between the dielectric and the electrode; (ii) space charge injected from the electrodes; (iii) space charge caused by migration of charge carriers over microscopic distances; (iv) electronic or ionic dipoles caused by migration of charges over microscopic distances, and (v) orientation of permanent dipoles¹⁵. Broad peaks represent the presence of multiplicity of relaxation mechanism. The multiplicity of relaxation in doped PMA may be because of the presence of trapping levels of different depths. Two peaks were reported for PMA. The first peak reported at 40°C (related to the charging temperature) and at 60°C due to the release of the charges trapped at crystalline/amorphous boundaries. PMA is a polar polymer; contribution to the polarization may be due to the alignment of dipoles and formation of space charge/injection of charge carriers from metal electrode under the effect of the electric field. β -Peak in polar polymers like PMA mainly arises from localized rotational fluctuations of the dipoles and therefore, it is also referred to as dipolar relaxation process¹⁶⁻¹⁷. The molecular mechanism of β -relaxation has been discussed by many groups¹⁸. In doped PMA β -relaxation can be associated to the dipole orientation of the polar side group. The occurrence of β -relaxation can be observed from certain characteristics of β -peak such as: (i) activation energy associated with this peak (Table 2) is very close to theoretically predicted value of E (i.e., ~0.20-0.50eV) and (ii) the peak position and activation energy do not change with poling field, but it strongly depends upon poling temperature. The high temperature

peak (α -peak) is due to the significant injection of charge carriers from the electrodes to the surface of the dielectric, which are frozen-in during the polarization of the specimen. It is also possible that doped PMA contains a high number of impurity molecules prior to the field treatment and these molecules are dissociated into various ionic species. Therefore, it is reasonable to attribute the peaks appearing in high temperature region to space charge relaxation process (i.e., α -relaxation). α -relaxation process occurs due to the injection of charge carriers from the electrodes at the metal polymer interface. The origin of α -relaxation process of this peak is confirmed by the facts: (i) peak current varies linearly with $E^{1/2}$ (Figure 3) and (ii) the activation energy for this peak (i.e., 0.5-0.9 eV) does not differ much for activation energy values reported for α -relaxation in many polymers¹⁹. The charge trapping in a polymer takes place at the molecular chain, the side chain and at the interface of the crystalline and amorphous regions of the polymer²⁰. The high field applied during electret formation may also produce some additional trapping sites. The charge release from these traps occurs because of thermal excitation and motion of the molecular chain that cause the lowering of trap's depth. The released charge can recombine, retrapped in trapping sites, or may become discharged at the electrodes. The high values of activation energies observed can only be associated with the ionic and electronic trapping²¹. The linear dependence of peak currents of β -peak and α -peak versus poling field (Figure 4) indicates that low temperature peak (β -peak) possesses dipolar nature and high

temperature peak (α -peak) possesses the space charge phenomena²². In present study, at higher temperatures the charge carrier injection increases, resulting in an increase in space charge and, hence, a rise in the current and since the polarizing field is kept constant the charge released from the impurity centres present in the sample does not neutralize the space charges thus yields increasing linear nature for peak currents of α -peak²³. As shown in Figure 5 linear relationship between T_m and T_p in the temperature region of the α -peak, suggests that the peak is due to the bulk effects²⁴.

Figure No. 6 shows the thermally stimulated discharge conductivity (TSDC) thermogram ($\log \sigma$ v/s $10^3/T$) plot for tri substituted ethylene glycol doped PMA at polarizing field i.e. 100kv/cm. When we plot $\log \sigma$ versus $1/T$, a straight line with a negative slope was obtained which indicates that as temperature increases conductivity increases as per Arrhenius equation

$$\sigma = \sigma_0 \exp (-E_a/KT),$$

Where σ_0 is the pre-exponential factor, E_a the activation energy of conduction and K the Boltzmann's constant. As the temperature increases polymer becomes soft and mobility of the main chain segments as well as the rotation of side groups become easier. Thus, at higher temperature more and more dipoles are oriented resulting in the higher equivalent surface charge density i.e as temperature increases conductivity increases. The values of activation energy have been calculated from the Arrhenius plot using the above relation (Table 3) & find that activation energy is different for different temperatures i.e for lower temperature activation energy is

high while for higher temperature activation energy is low. Conduction in lower temperature region takes place by thermal activation of carrier from one disordered state to another. At higher temperature, the trap is immobilized because of segmental chain motion or entire chain motion and agrees well with that reported²⁴. This could only be explained if we assume that dopant molecules when present in sufficient quantity form a link between trapping centres (here tri substituted ethylene glycol, has an electron donating hydrocarbon group which may act as a trapping centre for charge carrier) because of increased orbital overlaps. These experimental findings lead one to understand that steric effects in polymeric charge transfer complex play an important role. In polymer system, the acceptor cannot get close to the donor^{25,26}. It seems likely that in many polymeric charge transformation systems, the bulky nature of the groups and their close proximity to the polymer backbone will prevent the maximum interaction and stocking of acceptor layers is characteristic of the highly conducting Poly(methyl acrylate) Figure 7 illustrates the influence of the reaction time on polymerization of methyl acrylate. Polymerization percentage increases in value with increasing the reaction time first. However, the prolonged reaction time does not improve them after 1.5 hour. The reason can be attributed to the following fact that the reaction is carried out in alkali medium, the amount of the hydrolysis of carbonyl group increases with the prolonged time and leads to the decrease of pH. So, prolonging the reaction time obtains the similar results in contrast with the reaction temperature. Figure 8 demonstrated the SEM micrograph

of cellulose doped PMA. It can be seen that the atomic spacing for doped PMA is 100 micrometer which shows a broadening of the dielectric a relaxation spectrum with increasing cross-linking density, rationalized in terms of large and small-scale movements. The FT-IR spectra obtained for doped Poly (methyl acrylate) is shown in figure 9. In the IR spectrum of monomer, a characteristic carbonyl peak (C=O stretching) is at 1712 cm^{-1} . The peaks for the C=C was observed at 1638 cm^{-1} and at 935 cm^{-1} . The peaks in the range of $2900\text{--}3000\text{ cm}^{-1}$ correspond to the aliphatic C-H stretching. The -CH₂- peak is at 1410 cm^{-1} . The peak at 3415 cm^{-1} corresponds to O-H stretching. Furthermore, O-H bending was observed at 1298 cm^{-1} . The ester peak (C-O stretching) of monomer can be seen at 1200 cm^{-1} . In the spectrum of PMA, C=O bond stretching appeared at 1719 cm^{-1} . Also an aliphatic C-H stretching was observed at 2946 cm^{-1} and an aliphatic C-H bending (-CH₂-) at 1447 cm^{-1} . The broad peak at 3500 cm^{-1} corresponds to O-H bond stretching and also O-H bending can be seen at 1394 cm^{-1} . The ester peak of polymer was observed 1162 cm^{-1} . Peaks belong to double bond were completely disappeared. It can be concluded from IR spectra investigation that polymer was successfully achieved and the polymerization proceeds by carbon-carbon double bond opening. NMR Spectra of doped PMA polymeric thin film shown in figure 10 which shows the environment of doped polymer which includes 3 methyl groups at terminal position, 6 -CH₂ groups in between 8 aromatic & 13 aliphatic which shows the stiochoimetry of the polymeric substance as well as its Skelton. This confirmation is important because the

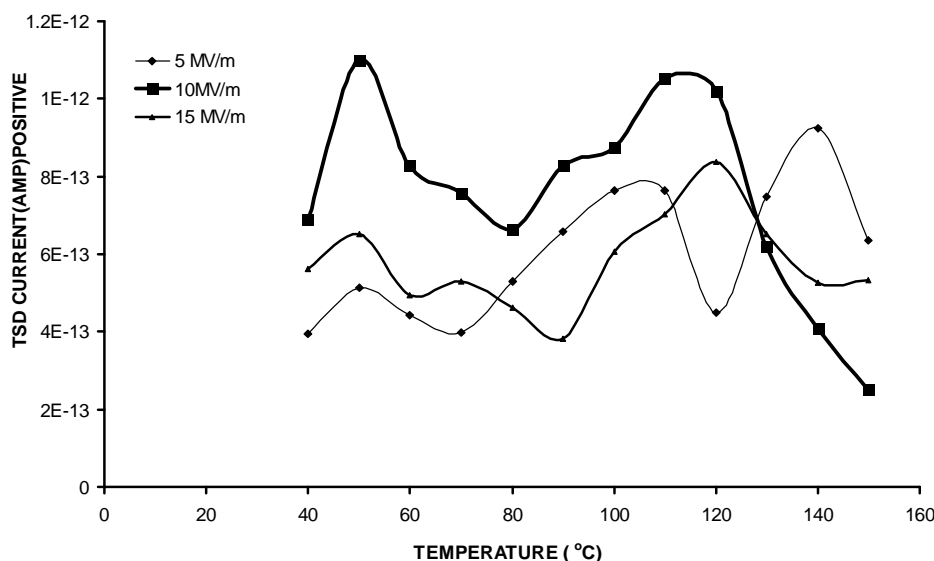


Fig 1- Thermally Stimulated depolarization Current thermograms for doped PMA at constant polarising temperature ($T_p=40^\circ\text{C}$) with various polarizing fields (05, 10 and 15 MV/m)

aromatic unit will confer conductivity to the doped PMA. The DSC measurements were carried out at N_2 atmosphere by heating polymer samples in the temperature range of -150 to 300°C . Thermograms of samples were shown in figure 11. No melting peak of polymer was observed due to the amorphous structure. The values are given in plot. The thermal stability of PMA samples were also characterized by means of TGA from 30°C to 600°C in N_2 atmosphere as illustrated in Figure 10. From the TGA thermograms, two measured weight losses were seen for bulk PMA's in which gamma and BPO were used as initiator. The thermograms are typical for acrylate polymers that thermal degradation is in the form of depolymerization. The small peak at 402°C for polymerization by radical initiator and a similar broad peak for polymer obtained by γ -radiation show the degradation of oligomers and/or residual

monomer that may exist in cross linked polymer. This peak is not observed for polymer obtained by solution polymerization. The main decomposition peak is much sharper and appears at lower temperature for the polymer obtained in solution. The broad peaks and higher temperature in first two figures show higher molecular weights and crosslinking or larger dispersive index of polymers. It is be concluded from the earlier result & discussion that the Poly(methyl acrylate) addition to ethyl glycol increase the covalence of bonds, the density & particle size which led to increase of electrical conductivity and polymerization of TSD currents. Shape & Size of TSDC Thermograms strongly dependent upon poling temp as well as poling fields. Commercially available polymer used in the present work is amorphous and the dopant used viz. tri substituted ethylene glycol, has an electron donating

hydrocarbon group which may act as a trapping centre for charge carriers. Finally, the individual TSDC relaxation peaks can also be used to obtain various numerical estimates of relaxation parameters. In

conclusion it would be appear from our work that TSDC is excellent complementary technique for investigating the electrical properties and is to be in agreement with the α -relaxation mechanism observed in PMA.

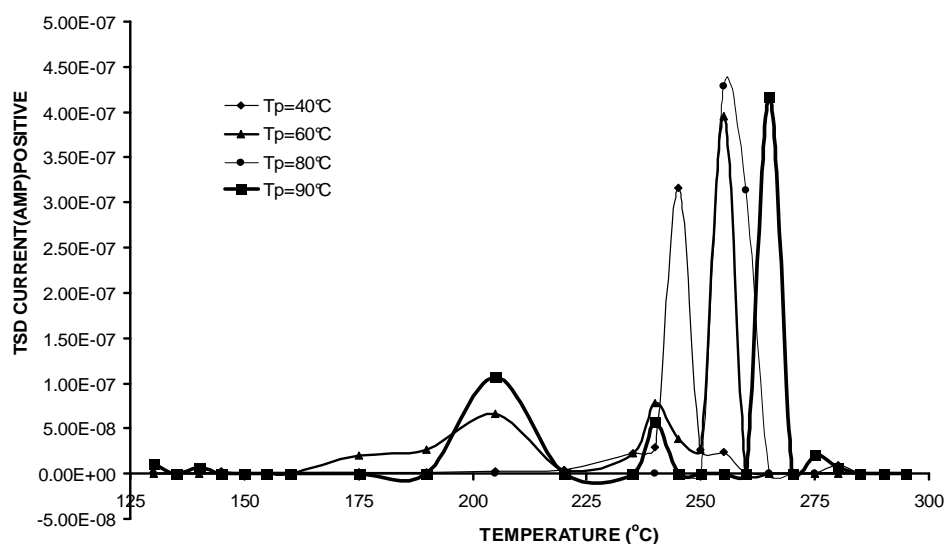


Fig 2: Depolarization vs. Temperature at constant polarization temperature (40,60,80 and 90°C) of doped poly methyl acrylate (PMA) for Al-Al system

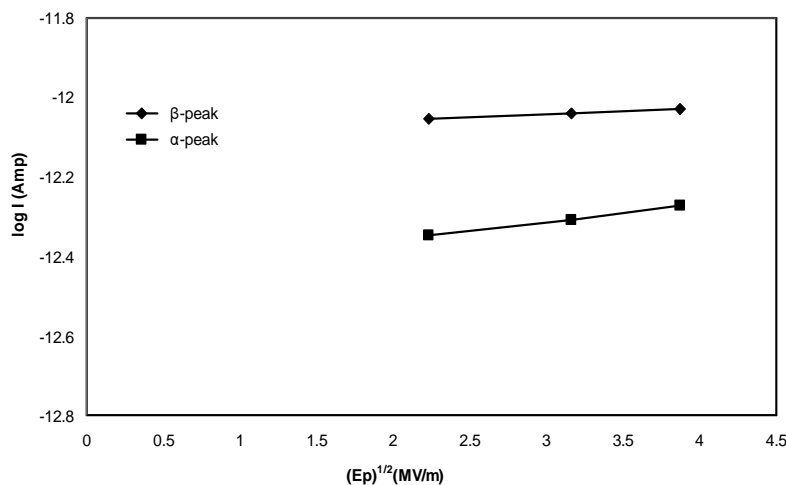


Fig 3: log I versus $(E_p)^{1/2}$ at constant polarising temp $T_p=60^\circ\text{C}$

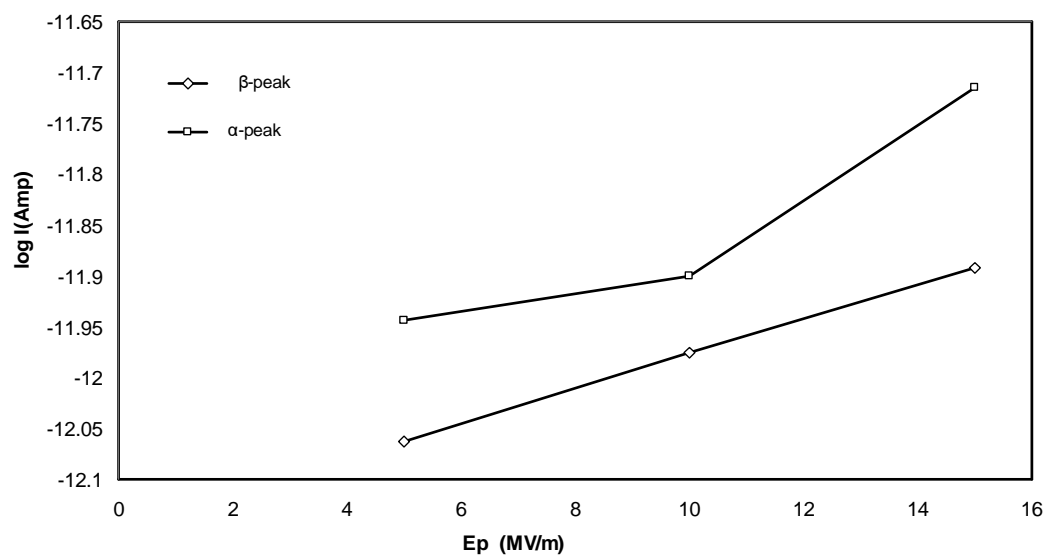


Fig 4: log I versus E_p at constant polarising temp. $T_p = 60^\circ\text{C}$

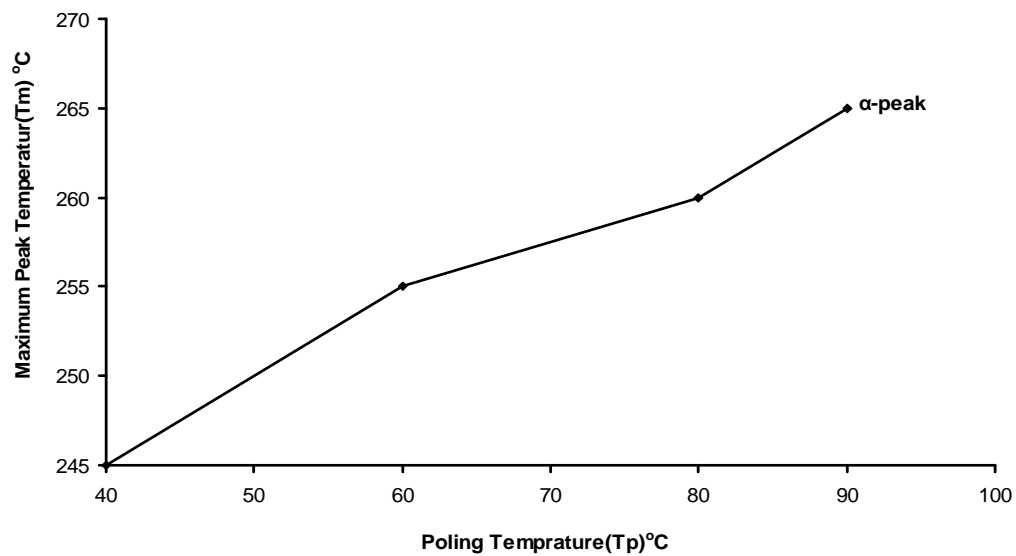


Fig 5: Poling temperature (T_p) versus maximum peak temperature (T_m) for doped PMA

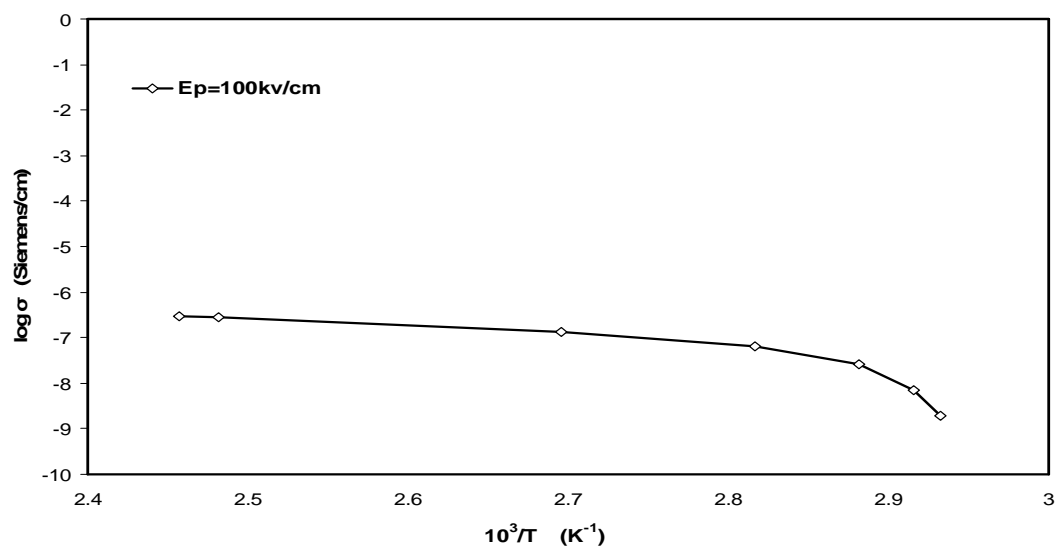


Fig 6: Arrhenius plot(Temperature dependence of conductivity for doped poly methyl acrylate(PMA) at given field)

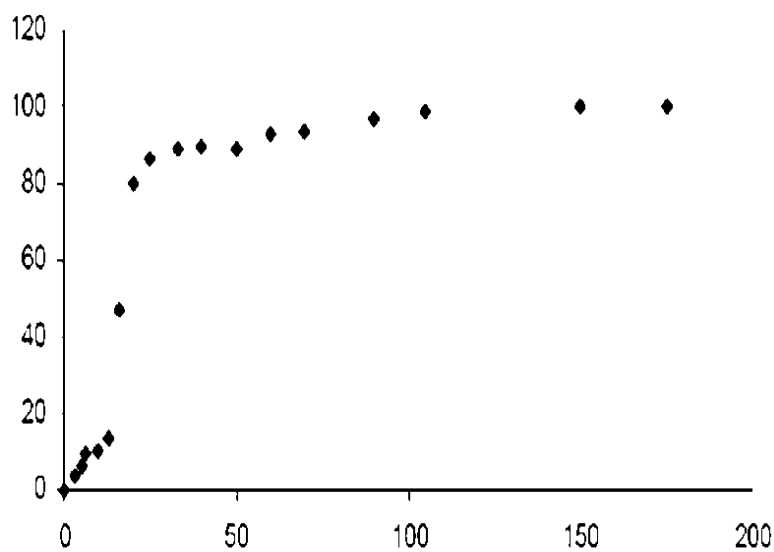


Fig 7: Monitoring of polymerization reaction of doped Poly Methyl Acrylate (PMA)

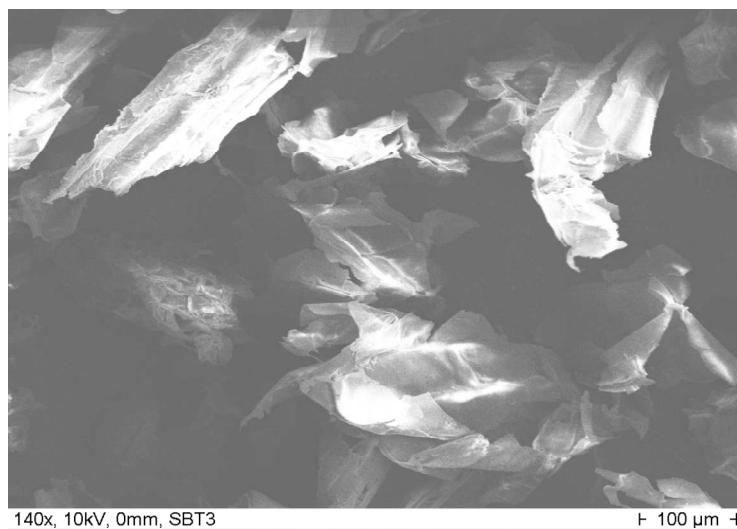


Fig 8: SEM images of doped Poly Methyl Acrylate (PMA) thin film

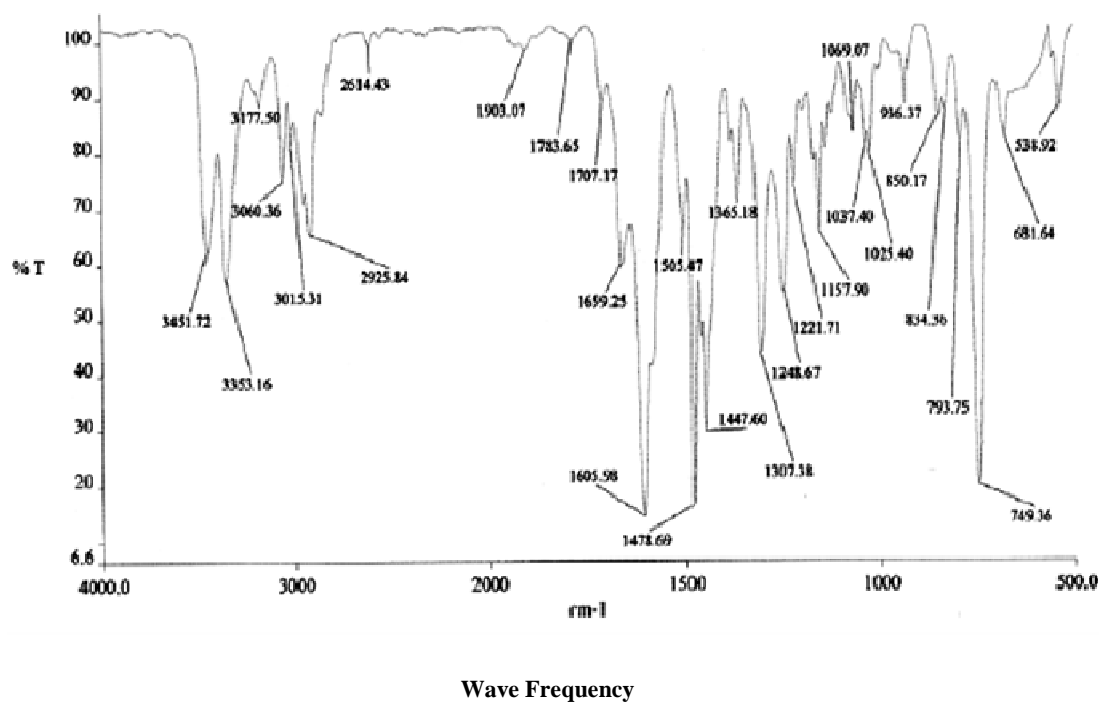


Fig. 9 : Infrared Spectroscopy of doped poly(methyl acrylate) (PMA) film.

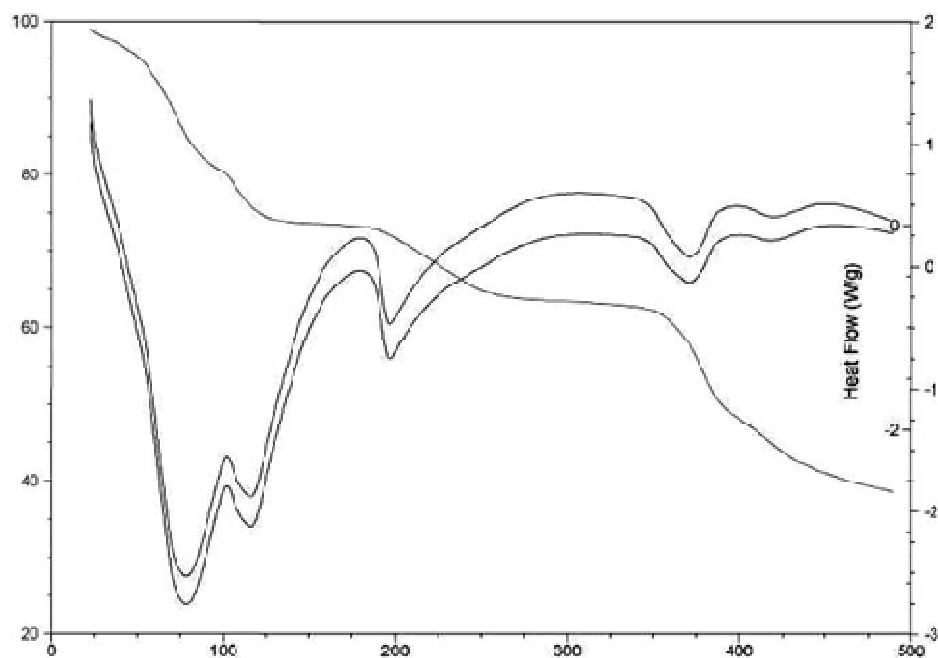
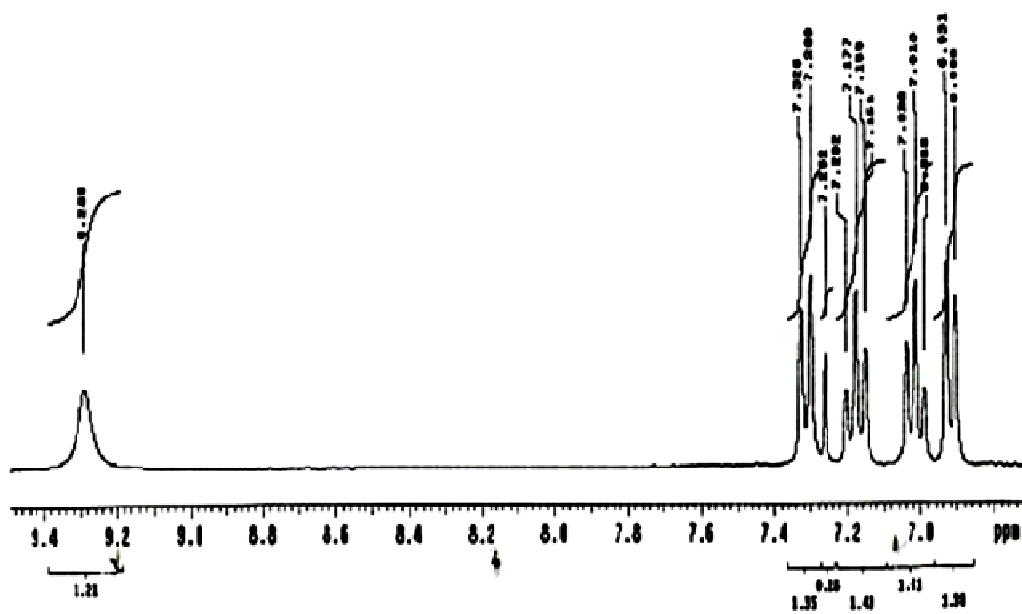


Table-1: Depolarization kinetic data for doped PMA samples at 40°C with various polarizing fields. Sample thickness 25µm for Al-Al System

Polari- zing Field	β -peak				α -peak					
(Ep) MV/m	Peak Current (Amp.)	Peak Temp. (°C)	Activation Energy (eV)	Relaxation Time(τ) (sec)	Charge Released Coul.(Q)	Peak Current (Amp.)	Peak Temp. (°C)	Activation Energy (eV)	Relaxation Time(τ) (sec)	Charge Released Coul.(Q)
05	5.1×10^{-13}	50	0.234	2.8×10^5	8.6×10^{-9}	9.2×10^{-13}	140	0.563	8.7×10^6	7.4×10^{-8}
10	1.09×10^{-12}	50	0.233	1.6×10^6	6.6×10^{-8}	1.07×10^{-12}	120	0.524	2.7×10^7	6.8×10^{-7}
15	6.5×10^{-13}	50	0.232	6.2×10^5	7.8×10^{-8}	8.3×10^{-13}	120	0.509	4.9×10^6	5.9×10^{-7}

Table-2: Depolarization kinetic data for doped PMA samples at a polarizing field 10MV/m with various polarizing temperatures i.e. 40, 60, 80 & 90°C respectively. Sample thickness 25µm for Al-Al System

Polarizing field Ep(MV/m)	Polarizing temperature Tp(°C)	Peaks	Peak temperature Tm(°C)	Activation energy E(eV)	Charge released Q(C)	Relaxation time τ (s)	Peak current Im (A)
10	40	β α	----- 245	----- 0.596	----- 4.5×10^{-9}	----- 2.1×10^4	----- 3.16×10^{-7}
10	60	β α	205 255	0.290 0.581	1.6×10^{-9} 3.3×10^{-8}	1.8×10^4 5.1×10^4	6.6×10^{-8} 3.96×10^{-7}
10	80	β α	----- 260	----- 0.573	----- 6.2×10^{-8}	----- 7.5×10^4	----- 3.14×10^{-7}
10	90	β α	205 265	0.280 0.554	5.3×10^{-8} 8.9×10^{-8}	2.3×10^4 7.8×10^4	1.07×10^{-7} 4.17×10^{-7}

Table 3 : Electrical Parameter i.e Electrical Conductivity & Activation Energy of doped PMA film at various temperatures & constant polarizing field $E_p=10\text{MV/m}$

Temperature ($^{\circ}\text{C}$)	Electrical Conductivity (σ)(Siemens/cm)	Activation Energy(E_a) (ev)
341	1.95×10^{-9}	0.64
343	7.08×10^{-9}	0.59
347	2.56×10^{-8}	0.52
355	6.26×10^{-8}	0.49
371	1.37×10^{-7}	0.46
403	2.85×10^{-7}	0.42
407	3.03×10^{-7}	0.37

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